

***Chapter 5: A Finite-difference-based Reactive  
Transport Model Assessment of the Effects of Ethanol  
Biotransformation on the Lengths of Benzene Plumes  
from Leaking Underground Fuel Tanks***

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## Summary

# (A Finite-Difference-Based Reactive Transport Model Assessment of the Effects of Ethanol Biotransformation on the Lengths of Benzene Plumes from Leaking Underground Fuel Tanks)

Groundwater modeling studies used to predict benzene plume behavior in the presence of ethanol have included several simplifying assumptions, including the following: (1) there will be preferential biodegradation of dissolved ethanol near the release source area, (2) no benzene degradation will occur within this ethanol degradation zone, (3) downgradient from the ethanol degradation zone, there will be a depletion of available electron acceptors that will result in lower benzene degradation rates, and (4) within the downgradient electron acceptor depletion zone, the benzene degradation rate is constant in time and space. These assumptions, if incorrect, would tend to overestimate predicted benzene plume lengths.

A more sophisticated modeling approach that better represents the spatial and temporal transport of electron acceptors is presented in this chapter. This modeling scenario treats the ethanol and benzene source terms as simple injection processes at a point; diffusion-limited partitioning out of a separate phase lens floating on top of the water table is not taken into account.

The modeling results suggest that:

- A four-fold decrease in the mean benzene biotransformation rate brought on as a consequence of ethanol biotransformation, and subsequent electron acceptor depletion, can potentially increase benzene plume lengths by a factor of roughly 2.5.
- This increase in benzene plume length is not inconsistent with the earlier findings using different modeling methodologies (McNab *et al.*, 1999), although it is somewhat toward the high end of the estimated plume length extensions explored.

A combination of more sophisticated reactive transport modeling (fully three-dimensional, with considerations of all plausible electron acceptor species) and additional constraints on reaction kinetics could be utilized in a future study to evaluate the plume lengthening phenomenon in more detail, taking into account the following:

- Diffusion of dissolved oxygen across the water table from vadose zone, which would likely act to suppress the increases in benzene plume lengths in many scenarios, since benzene plumes associated with nonaqueous phase liquids (LNAPLs) are likely to harbor the highest concentrations in the upper reaches of an aquifer.
- Dispersion of benzene and electron acceptors in the vertical dimension, both of which will serve to reduce the benzene plume length enhancement effect of ethanol.
- The effects of gas phase equilibria (carbon dioxide and methane) on aqueous phase oxidation-reduction geochemistry.
- The role of mineral phases, specifically Fe- and Mn-oxyhydroxides, in influencing oxidation-reduction geochemistry.



## **5. A Finite-Difference-Based Reactive Transport Model Assessment of the Effects of Ethanol Biotransformation on the Lengths of Benzene Plumes from Leaking Underground Fuel Tanks**

### **5.1. Introduction**

One of the principal concerns over the use of ethanol as a gasoline additive is the potential for increases in groundwater plume lengths of hydrocarbon constituents such as benzene should a release take place. This concern arises from two factors: (1) a binary water-ethanol mixture may result in a cosolvency effect that enhances the solubility of nonpolar organic compounds (such as benzene), and (2) the rapid biotransformation of ethanol can impede the biotransformation of benzene by reducing electron acceptor (e.g., dissolved oxygen, nitrate) availability. Although it may be possible to demonstrate these effects in laboratory-scale experiments, it is difficult to extrapolate the results to the field in a systematic way because the hydrogeology, biogeochemistry, microbial populations, and source release histories differ significantly from site to site. The ideal method for measuring effects of ethanol on benzene plume lengths in the field would be to quantify benzene plume lengths at sites where ethanol has been used as an additive and compare those to plume lengths from sites where there is no history of ethanol use. Unfortunately, sufficiently large databases to compare both classes of sites in the same hydrogeologic settings are not available. Moreover, although large databases for populations of fuel-hydrocarbon impacted groundwater sites exist (e.g., Rice *et al.*, 1995), delineating sites specifically associated with ethanol as a gasoline additive is difficult because of insufficiently documented inventory histories.

Given all of these constraints, mathematical modeling can be employed to explore plausible plume behavior scenarios. Previously, the effects of ethanol on benzene plume lengths were evaluated using a semi-analytical solute transport model that considered leaching of fuel constituents (ethanol, benzene) from a free-product lens on the water table using quasi-three-dimensional advective-dispersive transport, and simple, uniform first-order biotransformation (McNab *et al.*, 1999). This approach, implemented using a Monte Carlo scheme to assess parameter sensitivity, provided insights into the possible range in benzene plume length elongation that might be expected in association with ethanol. Nevertheless, an important shortcoming was that spatial and temporal variability in biotransformation rates as a result of electron acceptor depletion downgradient of the release was not taken into consideration. In this present study, a finite-difference-based reactive transport model is used to address this issue, thus serving as an addendum to the earlier 1999 study. The methodology behind the model and simulation results comparing hypothetical benzene-plus-ethanol and benzene-without-ethanol plumes are discussed below.

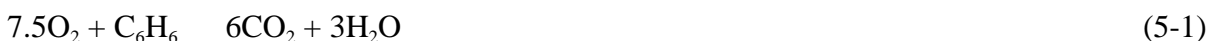
## 5.2. Methodology

Most closed-form analytical solutions of the solute transport equation are not capable of addressing spatial or temporal variability in the transformation term. Numerical models based on discretized flow domains are free from such restrictions and can be set up to handle arbitrary kinetic rate expressions so long as the spatial and temporal discretization are sufficient to provide an accurate approximation. For this study, a block-centered finite-difference model was assembled to simulate the transport and mutual biogeochemical interactions of fuel hydrocarbons (benzene and ethanol) and electron acceptor species (oxygen, nitrate, sulfate) as well as methane. The model uses a two-step algorithm where the transport equation is solved first for each species (in a flow field determined by an analytical solution) followed by the adjustment of chemical species concentrations within each volume element as a result of prescribed biogeochemical reactions. This modeling scenario treats the ethanol and benzene source terms as simple injection processes at a point; diffusion-limited partitioning out of a separate phase free-product lens floating on top of the water table is not taken into account. Biotransformation rates are assumed to follow a first-order kinetic rate law.

Four separate simulations were conducted, based on whether ethanol was present or absent in the gasoline mixture and whether benzene biotransformation rates were assumed to be spatially and temporally uniform or else depended on local biogeochemical redox zonation (which is influenced by the transformation of ethanol). The essential transport model parameters are listed in Table 5-1. The source term for the model consisted of a constant gasoline flux corresponding to 500 gal/yr (1893 L/yr) containing 1.5% benzene by volume and, in two of the simulations, 10% ethanol (EtOH) by volume. As an idealization, ethanol and benzene are assumed to be the only soluble components that are susceptible to oxidation and thus capable of imparting effects on electron acceptor concentrations.

The assumed first-order transformation rates for benzene,  $C_6H_6$ , in the four simulation scenarios are given on Table 5-2. In terms of specific electron-acceptor utilization mechanisms, four are assumed:

Aerobic respiration (oxygen reduction):



Denitrification (nitrate reduction):



Sulfate reduction:



Methanogenesis:





The reaction rates associated with these mechanisms reflect the declining energy gain realized by microorganisms as the most favorable electron acceptors are depleted and less energetically reactions must be called upon. The rates listed in Table 5-2 are consistent with those reported in the literature (e.g., Aronson and Howard, 1997). The reactive transport model tracks the sequential utilization of each electron acceptor within each volume element in the system and applies the appropriate rate constant.

Ethanol was assumed to biotransform via each of the mechanisms given in Equations (5-1) through (5-4) by analogous reactions. This was assumed to occur relatively rapidly, with a global first-order rate constant of  $0.1 \text{ day}^{-1}$ .

As a check on the accuracy of the transport simulation with the specified finite difference mesh, the results of the global transformation rate scenario with ethanol present (first-order transformation rate,  $\lambda$ , equal to  $0.002 \text{ day}^{-1}$ ) were compared with an analytical solution. Wilson and Miller (1978) proposed an analytical solution for solute transport in a homogeneous, infinite aquifer of constant thickness with a uniform fluid flow field, assuming an instantaneous point source. When integrated over time, the source term is transformed into one of continuous mass injection,

$$c(x, y, t) = \int_{\tau=0}^{\tau=t} \frac{M_f}{4\pi\phi\tau b\sqrt{D_L D_T}} \exp\left[-\frac{(x-vt)^2}{4D_L\tau} - \frac{y^2}{4D_T\tau} - \lambda\tau\right] d\tau \quad (5-5)$$

where  $M_f$  is the mass introduced per unit time,  $\phi$  the porosity,  $b$  the aquifer thickness,  $D_L$  and  $D_T$  the respective longitudinal and transverse dispersion coefficients,  $v$  the mean groundwater velocity,  $\lambda$  the first-order decay coefficient,  $x$  and  $y$ , the spatial coordinates relative to the source location,  $t$  the elapsed time between source introduction and sampling time, and  $\tau$  the variable of time integration. A comparison between the two models, based on the input parameters described in Table 5-1, indicates good agreement (Figure 5-1).

### 5.3. Results

Simulation results after 20 years are shown on Figures 5-2 through 5-7. The presence of ethanol creates a large anaerobic zone (Figures 5-2 through 5-5) that locally reduces the rate of benzene biotransformation. The result is a significantly larger benzene plume than would be expected otherwise (Figure 5-6). These simulation results pertain only to the constraints posed by the example problem and thus should not be extrapolated in a quantitative sense to benzene + ethanol plumes under the broad spectrum of hydrogeologic and release scenario conditions that may be encountered. Moreover, the assumption that benzene and ethanol are the only two soluble and oxidizable components of the gasoline mixture is obviously a gross idealization; other benzene, toluene, ethyl benzene, and xylene (BTEX) constituents and low molecular weight aliphatics will in reality also impact biogeochemical redox zonation. Nevertheless, the example is qualitatively quite reasonable and illustrates an apparent reduction in the overall rate of benzene biotransformation when ethanol is present.

## 5.4. Conclusion

While an earlier phase of the ethanol modeling focused on the separate phase dissolution issue and how this process may impact benzene plume length, this phase of the modeling looked in to spatial variability in the biogeochemical regime. The biogeochemical modeling results presented in this chapter suggest, *for the set of parameters used in the examples*, that a factor of 4 decrease in the mean benzene biotransformation rate brought on as a consequence of ethanol biotransformation, and subsequent electron depletion, increases benzene plume lengths by a factor of roughly 2.5. This number is not inconsistent with the earlier findings using different modeling methodologies (McNab *et al.*, 1999), although it is somewhat toward the high end of the estimated plume length extensions explored.

## 5.5. Recommendation

A combination of more sophisticated reactive transport modeling (fully three-dimensional, with considerations of all plausible electron acceptor species) and additional constraints on reaction kinetics could be utilized in a future study to evaluate the plume lengthening phenomenon in more depth, taking into account the following:

- Diffusion of dissolved O<sub>2</sub> across the water table from vadose zone, which would likely act to suppress the increases in benzene plume lengths in many scenarios, since benzene plumes associated with light nonaqueous phase liquids (LNAPLs) are likely to harbor the highest concentrations in the upper reaches of an aquifer.
- Dispersion of benzene and electron acceptors in the vertical dimension, both of which will serve to reduce the benzene plume length enhancement effect of ethanol.
- The effects of gas phase equilibria (CO<sub>2</sub> and CH<sub>4</sub>) on aqueous phase redox geochemistry.
- The role of mineral phases, specifically Fe- and Mn-oxyhydroxides, in influencing redox geochemistry.

## 5.6. References

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## ***Tables***



**Table 5-1. Essential solute transport modeling parameters.**

Parameter	Value
Groundwater velocity	$K = 3$ m/day $dh/dt = 0.002$ $\phi = 0.25$ $v = 8.8$ m/yr (via Darcy's law)
Dispersion tensor	$\alpha_L = 10$ m $\alpha_T = 1$ m
Aquifer thickness	$b = 10$ m
Source term	Vol. Flux of gasoline = 1893 L/yr Benzene content = 1.5% EtOH content = 10%
Background electron acceptor concentrations	$O_2 = 9$ mg/L $NO_3^- = 10$ mg/L $SO_4^{2-} = 20$ mg/L
Spatial and temporal discretization	$100 \times 50$ nodes ( $4m \times 4m$ cells) $\Delta t = 10$ days

**Table 5-2. Modeled biotransformation rate scenarios.  $\lambda$  denotes the first-order rate constant.**

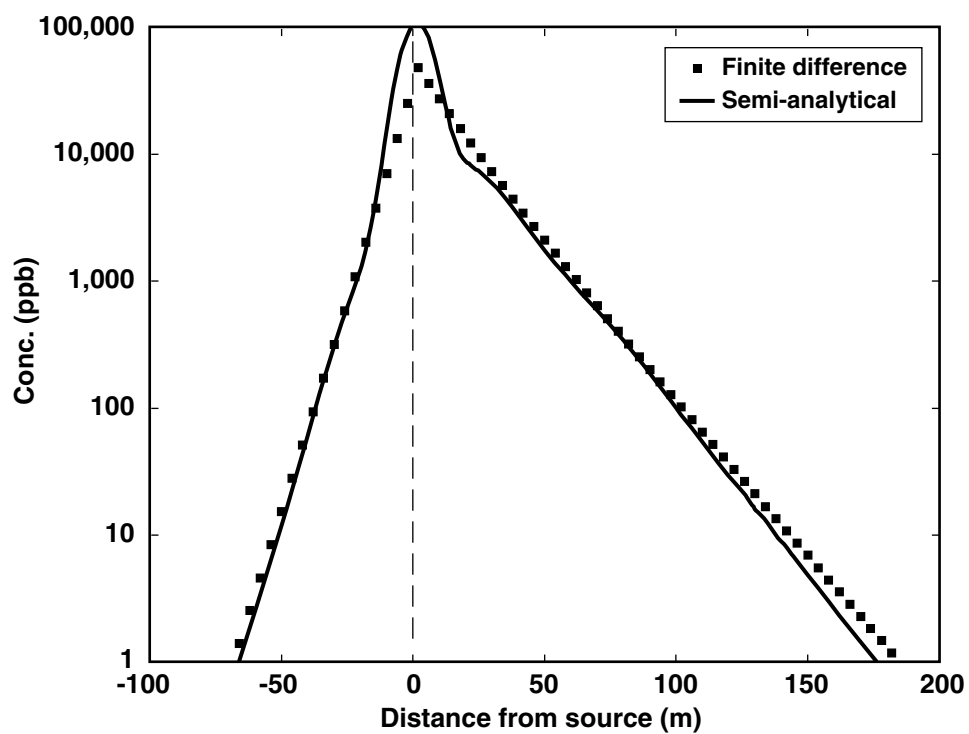
Scenario	Variable biotransformation rates, day <sup>-1</sup>	Global biotransformation rate, day <sup>-1</sup>
No EtOH	$\lambda = 0.01$ (for $O_2$ reduction) $\lambda = 0.003$ (for $NO_3^-$ reduction) $\lambda = 0.001$ (for $SO_4^{2-}$ reduction) $\lambda = 0.0005$ (for $CH_4$ production)	$\lambda = 0.008$
EtOH present (10%, by volume, in gasoline mixture)	$\lambda = 0.01$ (for $O_2$ reduction) $\lambda = 0.003$ (for $NO_3^-$ reduction) $\lambda = 0.001$ (for $SO_4^{2-}$ reduction) $\lambda = 0.0005$ (for $CH_4$ production)	$\lambda = 0.002$



## ***Figures***

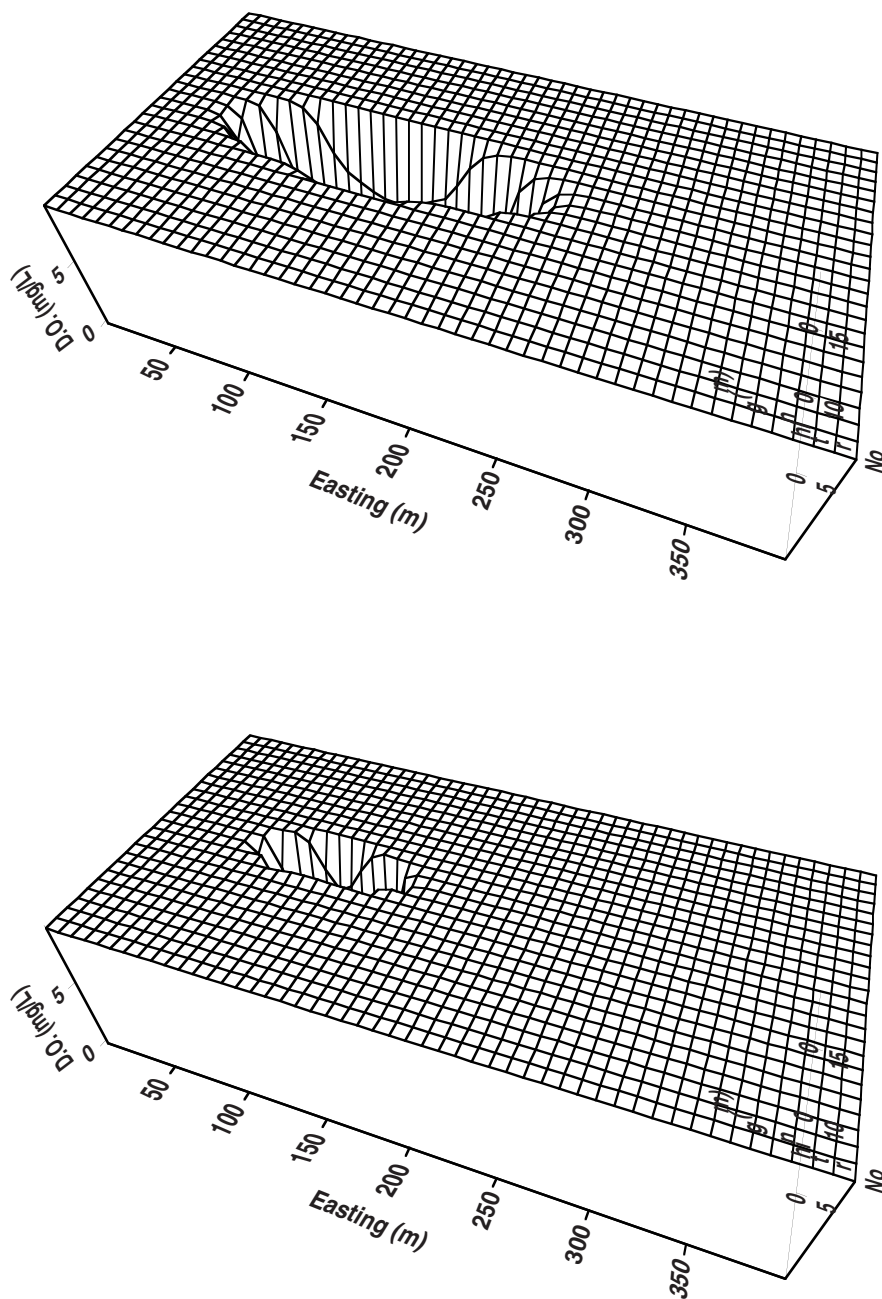






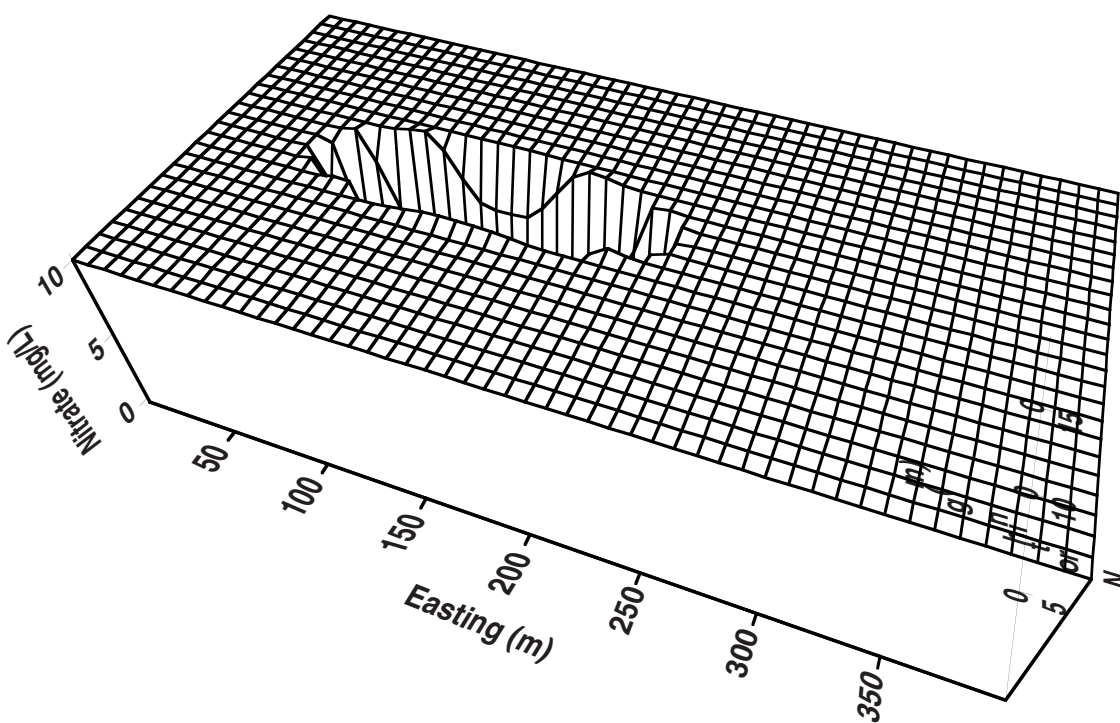
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**Figure 5-1. Modeled concentrations (numerical vs. analytical) of benzene along the longitudinal axis of the plume as defined by the input parameters given in Table 5-1.**



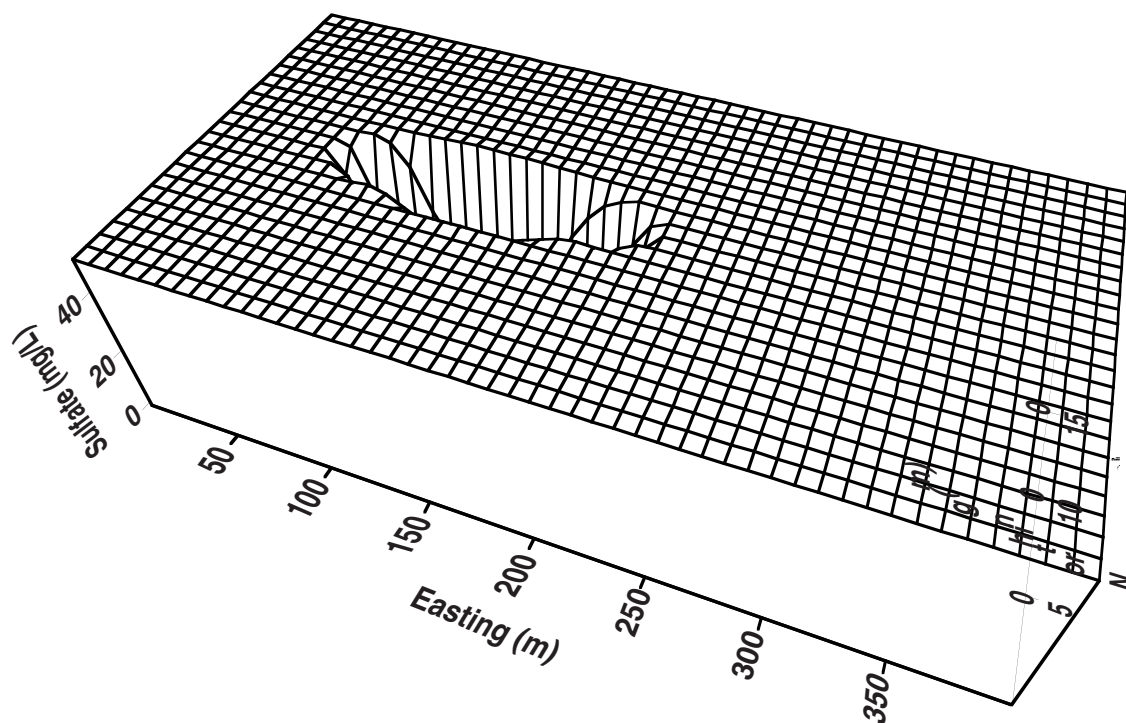
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**Figure 5-2. Redox zonation (dissolved  $O_2$ ) associated with a 20-year continuous release of gasoline containing benzene + ethanol (top) and benzene only (bottom). x-axis is 400 meters long; y-axis is 200. Vertical axis represents respective concentrations.**



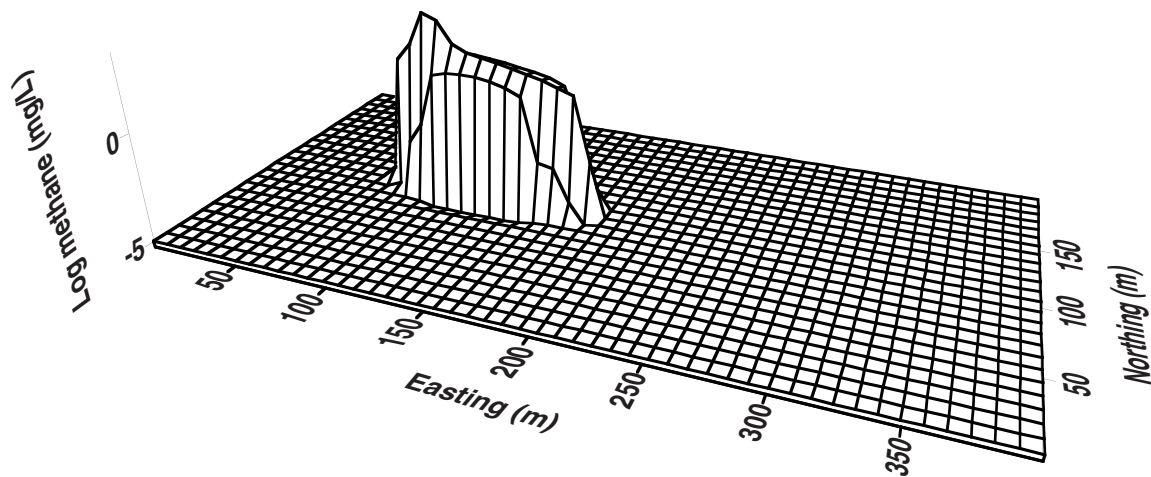
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**Figure 5-3. Redox zonation ( $\text{NO}_3^-$ ) associated with a 20-year continuous release of gasoline containing benzene + ethanol. x-axis is 400 meters long; y-axis is 200. Vertical axis represents respective concentrations.**



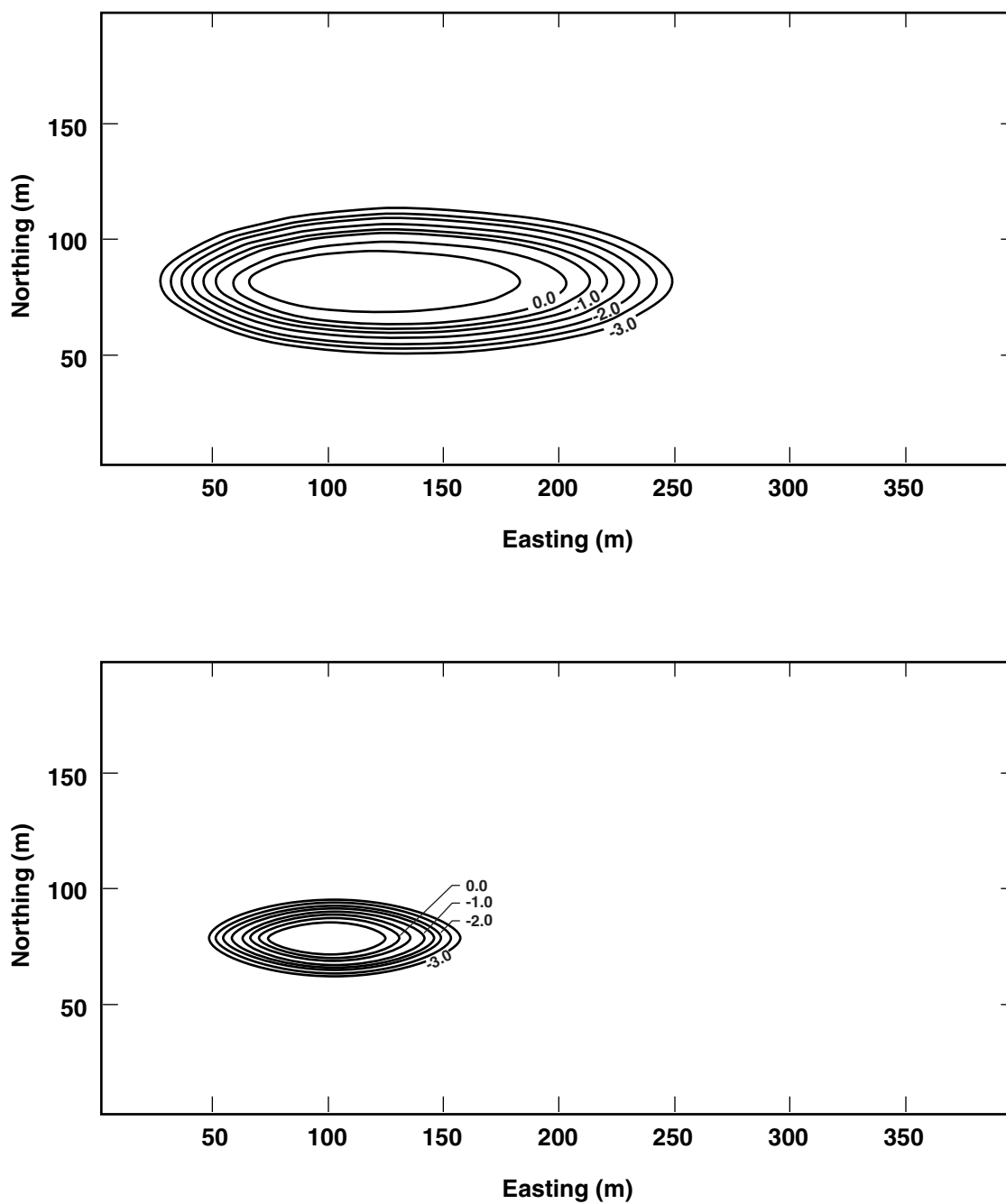
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**Figure 5-4. Redox zonation ( $\text{SO}_4^{2-}$ ) associated with a 20-year continuous release of gasoline containing benzene + ethanol. x-axis is 400 meters long; y-axis is 200. Vertical axis represents respective concentrations.**



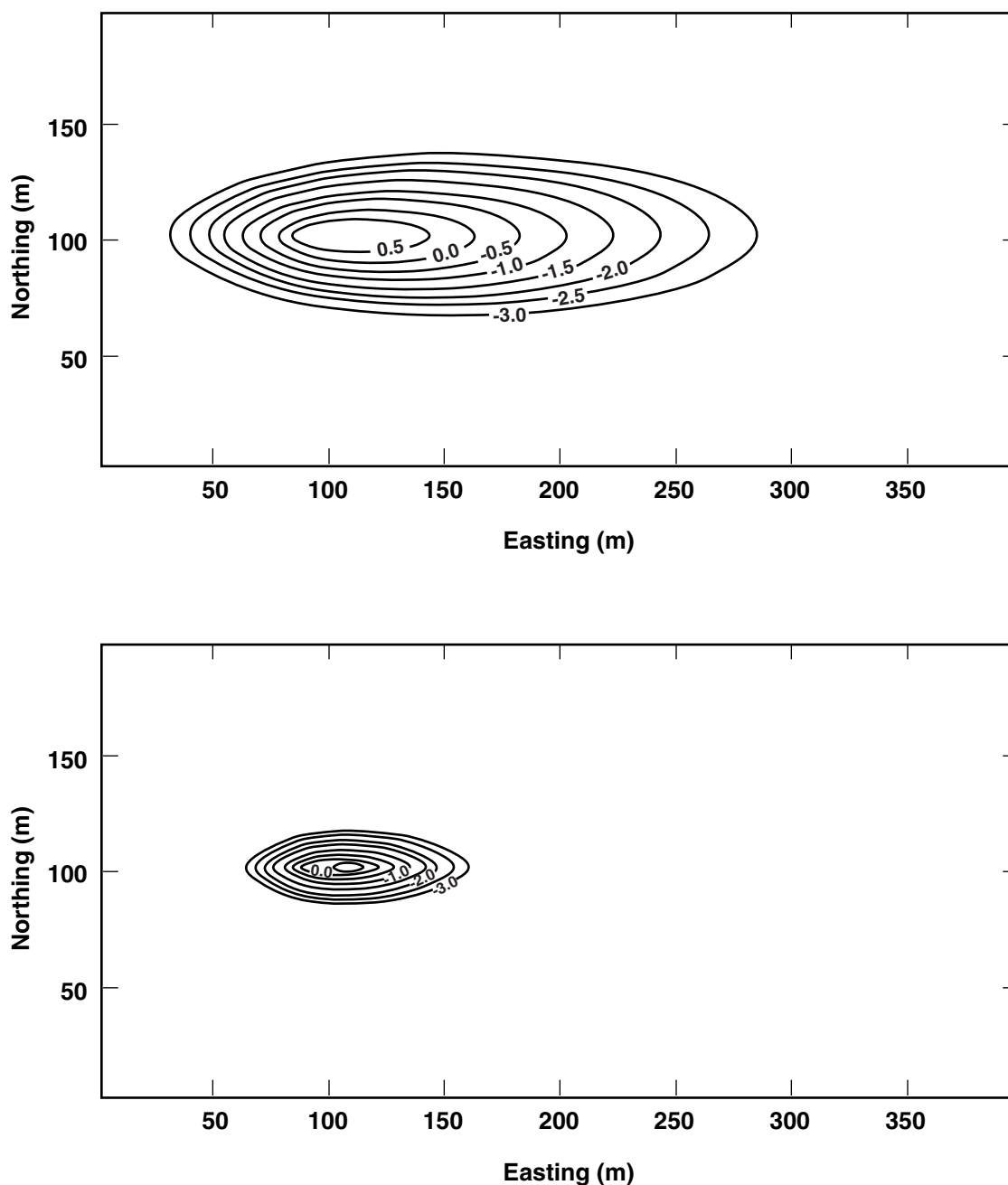
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**Figure 5-5. Redox zonation (CH) associated with a 20-year continuous release of gasoline containing benzene + ethanol. x-axis is 400 meters long; y-axis is 200. Vertical axis represents respective concentrations.**



ERD-LSR-01-0114

**Figure 5-6. The development of benzene plumes corresponding to model scenarios featuring benzene + ethanol (top) and benzene only (bottom). In both cases, the rates of benzene biotransformation depend on the local biogeochemical redox regime. Concentration contours are plotted logarithmically (with reference to concentration in parts per billion).**



ERD-LSR-01-0115

**Figure 5-7. Approximation of benzene concentrations using a global (i.e., spatially and temporally uniform) first-order rate constant corresponding to model scenarios featuring benzene + ethanol (top) and benzene only (bottom). By adjusting the global constants to 0.002 and 0.008 day<sup>-1</sup>, respectively, for the presence or absence of ethanol, the spatial extents of the plumes can be mapped effectively (compare to Figure 5-6). However, global values of  $k$  do not capture the spreading of high concentrations of benzene within the anaerobic plume interiors. Concentration contours are plotted logarithmically (with reference to concentration in parts per billion).**